

Uncertainty of heat capacity measurements with differential scanning calorimeters

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Abstract

The “Guide to the Expression of Uncertainty in Measurement” (GUM) is used to determine the uncertainty of heat capacity measurements by means of differential scanning calorimetry (DSC). The approach to the expression of uncertainty according to this guide gives a uniform basis for the comparison of experimental results, methods and instruments. On the basis of measurement results obtained with a power-compensated differential scanning calorimeter on a glassy ceramic and using common evaluation methods, an uncertainty analysis based on the “ISO Guide” is presented by an example. The relative expanded ($k = 2$) uncertainty of the heat capacity determination is $U(c_p)/c_p = 1.5\%$. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Heat capacity; DSC; Uncertainty determination

1. Introduction

“The statement of the result of a measurement is complete only if it contains both the values attributed to the measurand and the uncertainty of measurement associated with the value [2].”

Differential scanning calorimetry (DSC) is a commonly accepted method for the quantitative determination of heat capacities and enthalpies of phase transitions. Literature values of the uncertainty of heat capacity measurements obtained by this method give a non-uniform picture. For careful work with power compensation instruments, typical uncertainties of (3–5%) [3], 3% [4,5] and 1% [6] are reported. Optimistic estimations such as $\pm 0.25\%$ [7] for an achievable uncertainty, or 0.1% specifications [8] for the precision (repeatability) of specific heat capacity

measurements suggest that uncertainties can be achieved, which are comparable with those from high-precision adiabatic calorimetry. Unfortunately, these uncertainty specifications cannot be compared with one another, because the authors describe their interpretation of the uncertainty and their evaluation procedure in a closed and comprehensible way only in rare cases.

With the “Guide to the Expression of Uncertainty in Measurement” (GUM) [1], internationally accepted guidelines for evaluating and expressing the uncertainty of measurement results were published. This approach to the expression of uncertainty provides a uniform basis for the comparison of experimental results, methods and instruments. This guide was therefore used for the determination of the uncertainty of heat capacity measurements by DSC.

As an example, measurements for the determination of the specific heat capacity of a glassy ceramic have been chosen.

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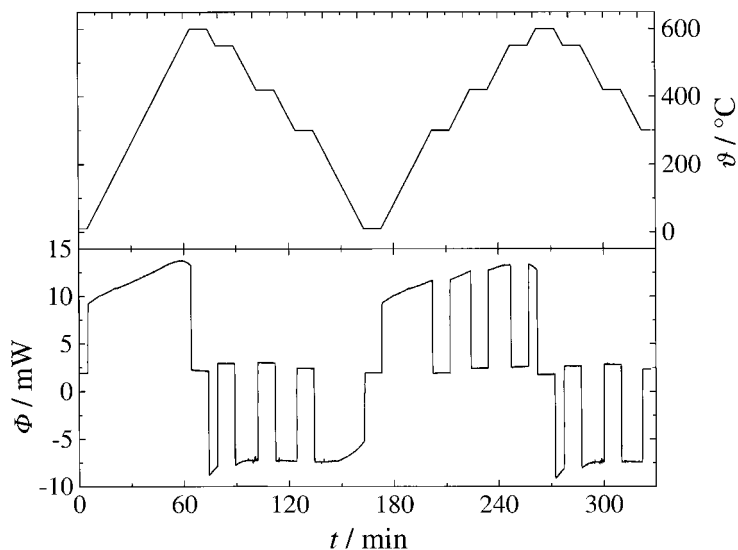


Fig. 1. Temperature program $\vartheta(t)$ and heat flow rate $\Phi(t)$ during sample measurement.

2. Measurement procedure

The measurements were carried out with a Perkin-Elmer DSC-2 (Norwalk, CT, USA) with a data acquisition and instrument control unit of IFA GmbH (Ulm, Germany) in the temperature range between 0 °C and 600 °C. The scanning rate β , was 10 K min⁻¹. Fig. 1 shows an example of the temperature program and the resulting heat flow rates. For the correction of the non-linear heat loss differences, additional intermediate isotherms were used [4]. The equation for the calculation of the specific heat capacity $c_{p,s}$ of the sample is given by

$$c_{p,s} = \frac{m_{\text{cal}} \cdot (c_{p,\text{cal}} + \delta c_{p,\text{cal}})}{m_s} \times \frac{(\Phi_s + \Delta\Phi_s) - (\Phi_0 + \Delta\Phi_0)}{(\Phi_{\text{cal}} + \Delta\Phi_{\text{cal}}) - (\Phi_0 + \Delta\Phi_0)} \quad (1)$$

The heat flow rate Φ , to temperature ϑ , assignment for sample (s), calibration sample (cal) and empty (0) measurement have been considered by a $\Delta\Phi$ correction. The $\delta c_{p,\text{cal}}$ term reflects the uncertainty of additional measurements on the calibration sample (sapphire supplied by Netzsch Gerätebau, Selb, Germany) in order to ensure traceability to NIST (National Institute of Standards and Technology, Gaithersburg, MD, USA) SRM-720 sapphire. In this work, the symbol Δ and the symbol δ are used to

denote the correction terms. The symbol Δ means a non-zero correction and δ a zero correction; both corrections having a non-zero uncertainty contribution.

The mass of the sample m_s and the mass of the calibration sample m_{cal} were determined using a microbalance (M 500 P, Sartorius, Göttingen, Germany). The uncertainty of the weighting was determined in accordance with [9] and is given in Table 2.

3. Temperature calibration

In DSC measurements, the temperature measurement acts in a dual manner as source of measurement uncertainties. One contribution is made by the assignment of the measured heat capacity to the sample temperature and the other by the fact that DSC is a comparative method. For this method, a calibration material with known specific heat capacity is needed to carry out the heat flow rate calibration. In other words, the unknown heat capacity of the sample is determined by comparison with a sample of known heat capacity (calibration sample).

Even though both samples are measured using the same temperature program, sample temperatures

occurring at the same time are often different because of the different thermophysical properties of the sample and the sample.

In this work, the influence of the temperature measurement is treated as a heat flow rate uncertainty stemming from incorrect temperature to heat flow rate assignment. The temperature calibration for this measurement series was a two-step procedure.

1. Calorimeter calibration by melting of indium, zinc and lithium sulphate (three-point calibration) at different heating rates and extrapolation to zero heating rate [10]. This first step of the temperature calibration procedure with extrapolation to zero heating rate provides the instrument calibration under steady-state conditions. It is obvious that the number and distribution of calibration points and interpolation method influence the uncertainty of the temperature calibration. Fig. 2 shows a typical temperature calibration by means of In, Sn, Pb, Zn and Li_2SO_4 .

In the case of the multi-point calibration shown, interpolation between the calibration points was carried out by a polynomial fit of third-order (solid line). The resulting uncertainty of the temperature measurement is a superposition of the uncertainties of calibration and interpolation. In this case, a visual test (Fig. 2) shows already that the

uncertainty due to interpolation is negligible in comparison with the repeatability of the calibration.

But, if a two-point temperature calibration is used, the uncertainty due to interpolation must be taken into account. The dotted lines show the systematic errors of temperature measurement due to the linearisation ($\Delta\vartheta_{\text{lin}}$) when two-point temperature calibration and three-point calibration are used. In this work, three-point temperature calibration with linear interpolation between either of the two points was applied.

2. The second step of the temperature calibration procedure is the thermal lag correction of sample and sapphire measurements via an enthalpy determination [6] at the start and at the end of a run. For correct assignment of the measured heat flow rate to the sample temperature under dynamic conditions, the heat transfer between the temperature sensor and sample surface and within the sample must be taken into account. The thermal lag is a measure of the temperature difference between the temperature sensor of the instrument and the mean sample temperature under dynamic (measurement) conditions.

The thermal lag determination is based on the assumption that in an ideal calorimeter after starting

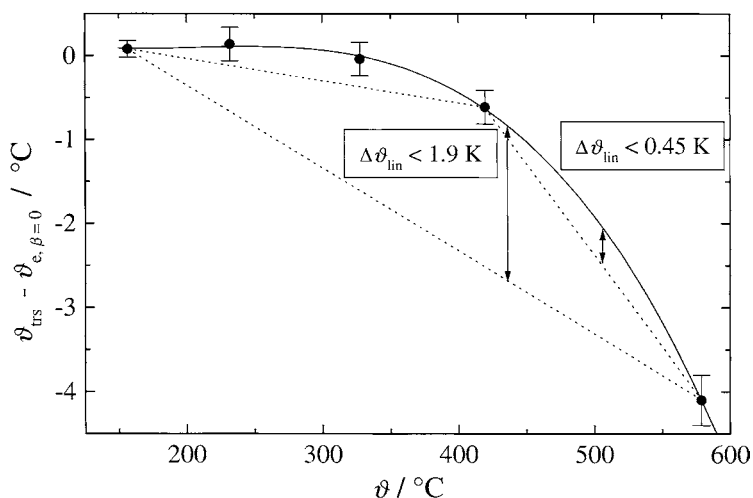


Fig. 2. Example of a temperature calibration of the calorimeter [10]. Difference between the extrapolated peak onset temperature $\vartheta_{e,\beta=0}$ and the known phase transition temperature ϑ_{trs} of the material used for temperature calibration as a function of the “indicated” temperature ϑ of the calorimeter. The error bars correspond to the repeatability of the temperature calibration [10].

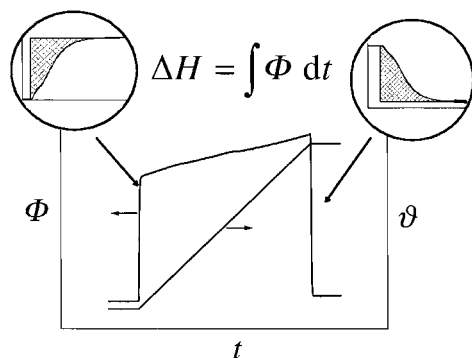


Fig. 3. Principle of the 'thermal lag' correction via enthalpy measurement.

or stopping of the temperature scanning, the heat flow rate should change in a step (Heaviside function). Deviations from this behaviour are produced by the heat transfer between the heater and the sample. The integration of the difference of the heat flow rate between measured and expected (stepwise) behaviour (Fig. 3) yields an enthalpy change ΔH of the sample after the scanning rate has been changed.

This thermal lag $\Delta\vartheta_{\text{lag}}$ (temperature lag) can be calculated according to

$$\Delta\vartheta_{\text{lag}} = \frac{\Delta H}{m_s c_{p,s}} \quad (2)$$

and is also a function of the scanning rate. For the calculation of the thermal lag, the heat capacities of the sample and reference sample (sapphire) must be known. The unknown heat capacity of the sample is determined in a first evaluation step without thermal lag correction. Because of the small contribution of the thermal lag correction, it is sufficient to use this heat capacity in the next evaluation step to correct the temperature to heat flow rate assignment.

In addition to [6], the thermal lag was determined both at the start and at the end of a measurement. It has been found that the thermal lag is temperature-dependent. It was, therefore, measured at all intermediate isotherms (Fig. 4).

These data were interpolated by an exponential decay function. The heat flow rate dependence of the thermal lag is taken into account by a linear function.

Table 1 shows the uncertainty budget for the sample temperature measurement at 500 °C, which is given by

$$\vartheta_s = \vartheta + \delta\vartheta_{\text{mat}} + \Delta\vartheta_{\text{calib}} + \Delta\vartheta_{\text{lin}} - \Delta\vartheta_{\text{lag}} \quad (3)$$

If normal (Gaussian) distribution can be assumed for the measurand and the standard uncertainty $u(y)$ associated with the output estimate y is reliable enough, the standard coverage factor $k = 2$ is to be used. The assigned expanded uncertainty U of a measurement

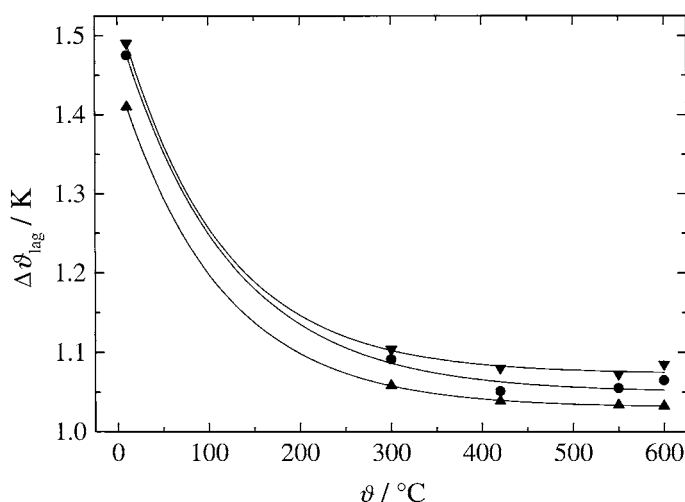


Fig. 4. Repeatability (three runs) of the thermal lag measurement and temperature dependence of the thermal lag $\Delta\vartheta_{\text{lag}}$ of the glassy ceramic at $\beta = 10 \text{ K min}^{-1}$.

Table 1
Uncertainty budget of the temperature measurement^a

Quantity, X_i	Estimate, x_i	Standard uncertainty, $u(x_i)$ (K)	Probability distribution	Sensitivity coefficient, $\partial\vartheta_s/\partial X_i$	Uncertainty contribution, $u_i(y)$ (K)
ϑ	500 °C	–	–	–	–
$\delta\vartheta_{\text{mat}}$	0.0 K	0.1	Normal	1.0	0.1
$\Delta\vartheta_{\text{calib}}$	1.9 K	0.3	Normal	1.0	0.3
$\Delta\vartheta_{\text{lin}}$	0.0 K	0.5	Normal	1.0	0.5
$\Delta\vartheta_{\text{lag}}$	1.0 K	0.2	Normal	1.0	–0.2
ϑ_s	500.9 °C	0.6			

^a ϑ_s : temperature of the sample; ϑ : temperature indication of the instrument; $u(\delta\vartheta_{\text{mat}})$: uncertainty of the certified melting temperature of the material used for the temperature calibration; $u(\Delta\vartheta_{\text{calib}})$: uncertainty of the temperature calibration and ‘measurement’; $u(\Delta\vartheta_{\text{lin}})$: uncertainty caused by the linearisation of the three-point calibration; $u(\Delta\vartheta_{\text{lag}})$: uncertainty of the thermal lag measurement.

corresponds to a coverage probability of approximately 95%.

The expanded uncertainty ($k = 2$) of the temperature measurement is $U(\vartheta_s) = 1.2$ K.

4. Heat flow rate calibration

For heat flow rate calibration sapphires from different sources (Perkin-Elmer, Netzsch, NIST) were used. The disadvantage of the NIST SRM-720 sapphire for heat flow rate calibration of DSC is its unfavourable geometry (rod of small diameter) resulting in inferior repeatability of the measurements in comparison to

disk-shaped samples from the other sources. Although a deviation of the specific heat capacity between the sapphires from Netzsch or Perkin-Elmer and SRM-720 had not been expected, comparison measurements were carried out (Fig. 5) to ensure traceability of the results. Fig. 5 shows the results of heat flow rate calibrations by means of sapphires from different sources, where K_ϕ is a factor for the correction of the instrumental heat flow rate calibration function.

Within the limits of the repeatability of heat flow rate measurements, no deviations between the different sapphires were found. Nevertheless, the resulting uncertainty contribution will be considered in the following paragraph.

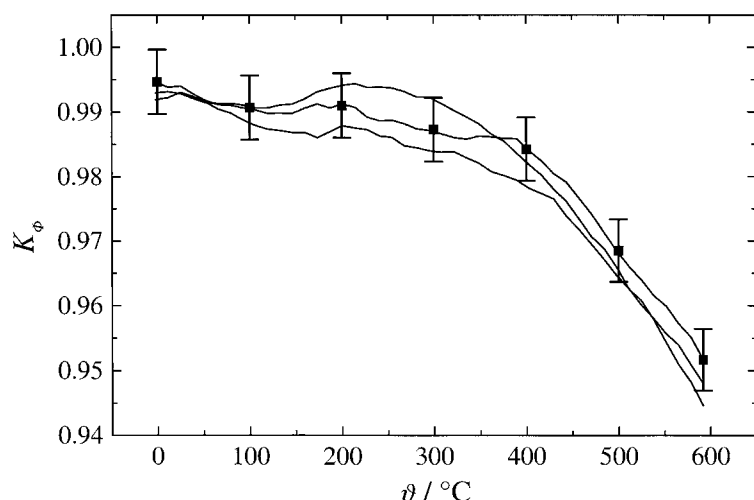


Fig. 5. Comparison of the heat flow rate calibration factor K_ϕ determined with sapphire from NIST and from two other suppliers as a function of temperature ϑ . The ‘error bars’ correspond to $\pm 0.5\%$.

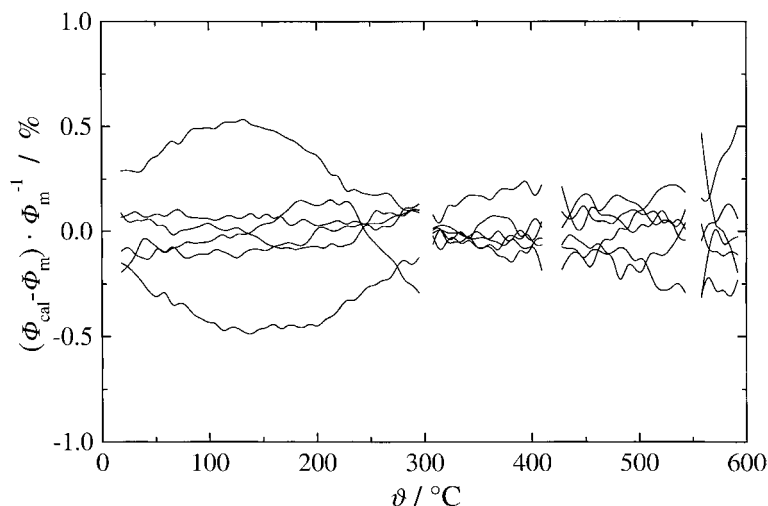


Fig. 6. Repeatability of heat flow rate calibrations as a function of temperature ϑ . Relative deviation of six measurements of the calibration sample Φ_{cal} in comparison to their mean value Φ_{m} .

Although the relative uncertainty of the specific heat capacity of the SRM-720 sapphire was certified by NIST to be $\pm 0.1\%$ (in a later examination [11] $\pm 0.05\%$ was stated), in the present work $\pm 0.2\%$ (with rectangular probability distribution) was assumed. The reason for this conservative estimation is that in the NIST certificate tabulated values are certified. But, many users utilise their own method for the interpolation (e.g. polynomial interpolation) between

these tabulated values. This can result in an additional uncertainty contribution.

For heat flow rate calibration, a sapphire sample of a heat capacity similar to that of the glassy ceramic sample was chosen.

It is well known that the repeatability of heat flow rate calibration (Fig. 6) and the repeatability of the sample measurement are the major contributions to the uncertainty of the heat capacity determination.

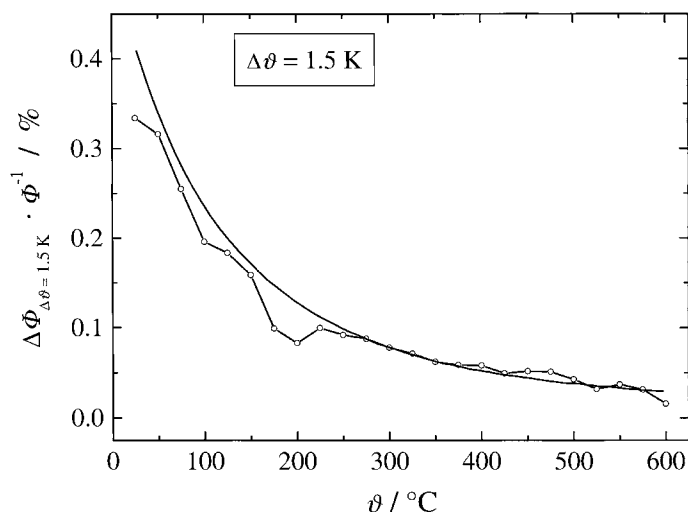


Fig. 7. Influence of a systematic deviation of the temperature measurement (e.g. $\Delta\vartheta = 1.5$ K) on the heat flow rate determination as a function of temperature: (○), glassy ceramic; (—), sapphire.

As a result of these measurements, a relative uncertainty of a (single) heat flow rate calibration was assumed to be $\pm 0.7\%$ on the assumption of rectangular probability distribution. Although the uncertainty of the heat flow rate calibration averaged over all calibrations would be considerably smaller, the uncertainty of a single measurement was used in the following for an uncertainty analysis for a typical measuring situation.

The influence of systematic deviations of the temperature measurement on heat capacity determination is a function of the difference and the temperature dependence of the heat capacities of the unknown sample and the calibration sample. To account for this, in the first step, the temperature calibration of the instrument is used to correct the measured temperatures. The next step is to consider the thermal lag. This gives a $\Delta\Phi$ correction for the measured heat flow rates Eq. (1). In the present work, the influence of the uncertainty of the temperature measurement is taken into consideration by the uncertainty of the $\Delta\Phi$ correction. This contribution depends on the temperature dependence of the measured heat flow rate and, consequently, also on the temperature dependence of the heat capacity of the sample and the calibration sample. Fig. 7 shows the relative heat flow rate deviation in case a systematic temperature measurement error of $\Delta\vartheta = 1.5$ K is assumed.

As the temperature dependencies of the specific heat capacities of the glassy ceramic and sapphire are almost identical, in this example, there is only a small contribution of the temperature measurement uncertainty to the uncertainty of the heat capacity determination.

5. Sample measurement

In DSC, a measurement normally consists of some single experiments (runs) only. As already mentioned in the previous section, the repeatability of these experiments is in most cases the major source of uncertainty. If only a single (or a small number of) experiment(s) is/are carried out, the problem is to get information about the uncertainty of the experiment.

One solution to this dilemma is to investigate the repeatability of heat capacity determinations for selected and representative samples and/or model materials. This has been done for sapphire ($\pm 0.7\%$,

Fig. 6), nickel ($\pm 0.6\%$) and the glassy ceramic ($\pm 0.8\%$). In the typical case of an unknown sample, it is also necessary to verify that the repeatability is equal to or better than that for a previously investigated model material/crucible combination. It is well known that the thermal contact between the sample, crucible and furnace and the sample/crucible positioning are of dominating influence in achieving good repeatability.

It has been found that two additional criteria can be used to test whether a single run fulfils the repeatability requirements. These criteria are the isothermal heat loss and the thermal lag. The isothermal heat loss $\Delta\Phi_{\text{iso}}$ is the (baseline corrected) heat flow rate offset between the initial and the final isothermal segment of a measurement. It is a measure of the heat flow rate asymmetry between the sample cell and reference sample cell in a twin calorimeter and characterises the additional heat conduction path via the sample [12]. Fig. 8 shows the typical temperature dependence of the isothermal heat loss.

Because the isothermal heat loss depends on various thermophysical properties and geometric dimensions of sample, crucible and measurement cell and the stability of the block-temperature, the prediction of the isothermal heat loss is difficult and uncertain. Therefore, the interpretation of the measured isothermal heat loss function is rather used in a qualitative manner. That means that deviations from the typical shape of that function (Fig. 8) are regarded as an indication that the assumptions about the repeatability of a measurement are not complied with. Outliers often give an indication why the results of the corresponding measurement deviate from the results of other measurements.

Provided that all measurements have been carried out with the same instrumental settings, the typical thermal lag to temperature relation depends on the following major contributions:

- the heat conduction path inside the sample cell;
- the thickness d and the thermal diffusivity a of the sample;
- the contact resistances between the sample cell and sample.

As the first and dominating part remains constant under these conditions, the measured thermal lag gives information about changes of the other ones. For typical instrumental settings, the prospective value

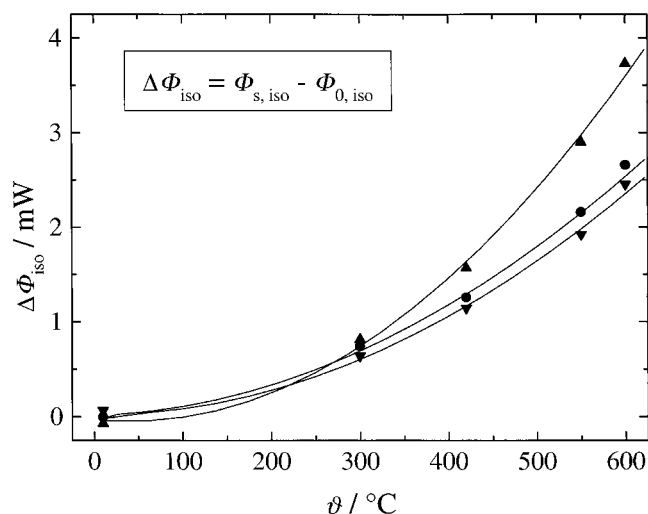


Fig. 8. Typical temperature dependence (three runs) of the isothermal heat loss $\Delta\Phi_{\text{iso}}$ during the measurement of the glassy ceramic.

of the thermal lag of the calibration sample measurement is known from former experiments and its measurement is therefore an independent test of the contact resistances. If the measured thermal lag (Fig. 4) of a measurement is inside a prescribed confidence interval (e.g. $\pm 10\%$), it is assumed that the repeatability of the measurement is within the limits of the model material/crucible combination.

The contribution of the heat conduction within the sample can be estimated from theoretical calculations. Here, the one-dimensional transient solution of the heat conduction equation for linear heating of the front face of the sample and adiabatic boundary conditions at the rear face of the sample [13] can be used. From this solution one can derive the following equation for the temperature difference between the mean sample temperature and the front face temperature in the case of quasi-steady-state conditions:

$$\Delta\vartheta = \frac{\beta d^2}{3a} \quad (4)$$

With this equation, a typical contribution of the sample (with $d = 1 \text{ mm}$, $\beta = 10 \text{ K min}^{-1}$) to the thermal lag between $\Delta\vartheta = 0.5 \text{ mK}$ (copper) and $\Delta\vartheta = 0.6 \text{ K}$ for polymer materials was estimated. The comparison with the measured thermal lag (1.0–1.5 K, Fig. 4) shows that with the exception of low thermal diffusivity materials (polymers), the thermal lag is domi-

nated by the heat conduction between the heater and the sample. For the sample measurement, the thermal lag determination can therefore be used as an independent test to also ensure sufficiently low thermal contact resistances. The thermal lag determination for the empty measurement does not provide relevant information; because of the symmetry of the system, the instrument control dominates the instrument response when the scanning rate is changed.

In this case, two approaches are possible. The first one is the use of rule-of-thumb thermal lag data from measurements on samples with negligible internal thermal lag. The other one is to carry out the subtraction of the empty measurement before the thermal lag correction of the sample measurement and calibration sample measurement. In this work, the first approach was used.

6. Uncertainty budget

The investigations have shown that the relative uncertainty of the specific heat measurement between 0°C and 600°C is not a function of temperature. The uncertainty budget for the specific heat capacity measurement has therefore been exemplarily calculated at a temperature $\vartheta = 250^\circ\text{C}$. Table 2 gives a summary of the results of this analysis.

Table 2
Uncertainty budget of the specific heat capacity determination

Quantity, X_i	Estimate, x_i	Standard uncertainty $u(x_i)$	Probability distribution	Sensitivity coefficient, $\partial c_{p,s}/\partial X_i$	Uncertainty contribution, $u_i(y)$ ($\text{J g}^{-1} \text{K}^{-1}$)
m_{cal}	55.41 mg	0.006 mg	Rectangular	$18 \text{ J g}^{-2} \text{K}^{-1}$	0.1×10^{-3}
$c_{p,\text{cal}}$	$1.060 \text{ J g}^{-1} \text{K}^{-1}$	$0.001 \text{ J g}^{-1} \text{K}^{-1}$	Rectangular	0.96	1.2×10^{-3}
$\delta c_{p,\text{cal}}$	$0.0 \text{ J g}^{-1} \text{K}^{-1}$	$0.003 \text{ J g}^{-1} \text{K}^{-1}$	Rectangular	0.96	2.9×10^{-3}
Φ_{cal}	11.09 mW	0.05 mW	Rectangular	$-100 \text{ s g}^{-1} \text{K}^{-1}$	-4.6×10^{-3}
$\Delta\Phi_{\text{cal}}$	-0.009 mW	0.003 mW	Rectangular	$-100 \text{ s g}^{-1} \text{K}^{-1}$	-0.3×10^{-3}
m_s	52.29 mg	0.006 mg	Rectangular	$-19 \text{ J g}^{-2} \text{K}^{-1}$	-0.1×10^{-3}
Φ_s	10.13 mW	0.05 mW	Rectangular	$110 \text{ s g}^{-1} \text{K}^{-1}$	5.3×10^{-3}
$\Delta\Phi_s$	-0.01 mW	0.003 mW	Rectangular	$110 \text{ s g}^{-1} \text{K}^{-1}$	0.3×10^{-3}
Φ_0	1.2 mW	0.1 mW	Rectangular	$-11 \text{ s g}^{-1} \text{K}^{-1}$	-1.5×10^{-3}
$\Delta\Phi_0$	-0.002 mW	0.0004 mW	Rectangular	$-11 \text{ s g}^{-1} \text{K}^{-1}$	-0.004×10^{-3}
$c_{p,s}$	$1.015 \text{ J g}^{-1} \text{K}^{-1}$	$0.008 \text{ J g}^{-1} \text{K}^{-1}$			

7. Conclusions

In the present work, the equation for the specific heat capacity determination by means of DSC used at Physikalisch-Technische Bundesanstalt (PTB, Braunschweig, Germany) is presented and the influence parameters are quantified. It was shown, that the thermal lag is considerably influencing the temperature determination and in which way this can be considered in the uncertainty budget. The results of the uncertainty analysis confirm again that the major source of uncertainty for DSC measurements is the repeatability of the heat flow rate measurement and calibration. The final relative expanded ($k = 2$) uncertainty of the specific heat capacity determination is given by

$$\frac{U(c_{p,s})}{c_{p,s}} = 1.5\%$$

with a reported result (exemplarily) at $\vartheta = 250 \text{ }^\circ\text{C}$

$$c_p = (1.015 \pm 0.016) \text{ J g}^{-1} \text{K}^{-1}$$

If the sapphire used for heat flow rate calibration is not a certified reference material, the traceability of the measurements will not be ensured and the uncertainty of the heat flow rate calibration will be questionable. It was shown how this gap can be closed with the consequence that an additional uncertainty contribution must be considered.

If the best ($U(c_{p,\text{cal}})/c_{p,\text{cal}} = 0.05\%$) certified reference material available for the heat flow rate calibration is used, the relative uncertainty of the specific heat capacity measurement will be reduced to $U(c_{p,\text{cal}})/c_{p,\text{cal}} = 1.4\%$.

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